

Dynamic light scattering studies on random cross-linking of polystyrene in semi-dilute solution

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Abstract

The random cross-linking of appropriately functionalized polystyrene in semi-dilute toluene solution ($c = 0.01\text{--}0.05$ g/mL) was studied by time-dependent measurements of dynamic light scattering. Macroscopic gelation occurred from concentrations as low as 0.02 g/mL. The gelation time, determined from the first appearance of fluctuations of the scattering intensity and the initial amplitude of the intensity correlation function (ICF), decreases markedly from about 100 min to 10 min with an increase of polymer concentration or cross-linker content. After the gel point, the ICFs display a characteristic power-law decay. The power-law exponent, $n = 0.75 \pm 0.06$, does not change with (i) extent of reaction, (ii) polymer concentration, and (iii) cross-linker concentration, within the inspected ranges. This universal behavior is traced back to the fact that gelation took place as a result of random cross-linking of existent macromolecules, whose state of solution does not change markedly during conversion.

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1. Introduction

Polymer gels are three-dimensional polymer networks swollen by solvent. They can be prepared by polymerization of multifunctional monomers or by cross-linking of existent polymer chains. Depending on whether the cross-links are formed by physical junctions or covalent bonds, the resulting network is termed a physical gel or a chemical gel [1].

A characteristic of the gelation process is the critical point (gel point) where the transition occurs from a sol, an assembly of branched structures of finite size, into a gel, where such structures span the whole sample [1–3]. From their rheological investigations on the gelation process of polydimethylsiloxane, Chambon and Winter [4] concluded that the storage and loss moduli at the gel point exhibit a frequency dependence

$G'(\omega) \sim G''(\omega) \sim \omega^{0.5}$. This relationship was later generalized to $G'(\omega) \sim G''(\omega) \sim \omega^n$, where $0 < n < 1$ [5]. Rheological measurements on incipient physical [6–11] and chemical [12–23] gels support this power-law behavior, although without strong universality of the viscoelastic exponent n . The viscoelastic exponent has been related to the fractal dimension of the growing clusters [22–26]. Experiments on the curing of epoxy resins show that the loss modulus exhibits the same power-law $G'' \sim \omega^n$ in the entire postgel regime up to the fully cured network, while the storage modulus becomes frequency independent [27–31].

Martin et al. [32,33] probed the sol–gel transition during the formation of silica gels by dynamic light scattering (DLS). They were the first to report on a power-law time decay of the intermediate scattering function, and they discussed a relationship with the power-law exponent found by rheology. Later, Shibayama and Norisuye [34] generalized this approach by fully considering the loss of ergodicity during the gelation process. Their treatment makes use of the fundamental

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analysis of DLS in non-ergodic media by Pusey and van Megen [35]. The theory was then used for the discussion of experimental data on colloids and gels [35–41].

Now, there are a large number of studies of gelation by dynamic light scattering [32–34,42–53]. The majority of these deal with gels made by cross-linking copolymerization of monomers and cross-linkers [34,42–45], by the sol–gel process (silica gels) [32,33,46,47], or by physical gelation [48–53]. In this work, we study the random cross-linking of existent polymer molecules in semi-dilute solution. Linear polystyrene was first randomly functionalized with aminomethyl groups. Cross-linking was subsequently achieved via the reaction with terephthalaldehyde in toluene solution. The course of the reaction was followed by time-resolved DLS.

2. Experimental section

2.1. Preparation of polystyrene gels

Polystyrene gels were prepared by cross-linking poly(styrene-*co*-aminomethylstyrene) [P(S-*co*-AMS)] with terephthalaldehyde in toluene solution. The P(S-*co*-AMS) was obtained as described previously [41]. It has a molar mass $M_w = 335\,000$ g/mol, $M_w/M_n = 2.1$, and the mole ratio of aminomethyl groups and repeat units of polystyrene is 1:27. The polymer may be considered a polystyrene with 3.7% of the repeat units being functionalized and randomly distributed along the chain.

Solutions containing 0.1–0.5 g of P(S-*co*-AMS) in 8 mL toluene ($\geq 99.7\%$, Sigma–Aldrich) were prepared. Likewise, solutions of 1.61–10.74 mg terephthalaldehyde (cross-linker) in 2 mL toluene were made. Corresponding solutions were filtered through a 1 μ m PTFE membrane directly into the dust-free light scattering cuvettes to obtain a total volume of 10 mL in each case. DLS measurements were started immediately thereafter in order to follow the gelation kinetics. Table 1 shows a listing of the samples prepared. A gel sample is denoted *Ga-b*, where *a* is the polymer concentration in 0.01 g/mL and *b* is the ratio of polymer repeat units and aldehyde groups of the cross-linker. The quantity $1/b$ is also denoted as cross-linker concentration.

Table 1
Preparation conditions of polystyrene gels

Sample no.	C_{PS} (g/mL)	C_{CL}^b (mol%)
G1-30 ^a	0.01	3.33
G2-30	0.02	3.33
G3-30	0.03	3.33
G4-30	0.04	3.33
G5-30	0.05	3.33
G5-50	0.05	2.00
G5-75	0.05	1.33
G5-100	0.05	1.00
G5-200	0.05	0.50

^a Only microgel formed.

^b Ratio of aldehyde groups of the cross-linker and polymer repeat units.

2.2. Dynamic light scattering (DLS)

Dynamic light scattering measurements were carried out at 25 °C on an ALV/DLS/SLS-goniometer with a multi- τ digital correlator 5000E (ALV, Langen, Germany). A solid-state laser (ADLAS DPY 135, output power $\cong 100$ mW at $\lambda_0 = 532$ nm) was used as the light source. The set-up is a classical one with pinhole collimation and one photo-multiplier.

To study the gelation kinetics, the scattering intensity was collected at a scattering angle of 90° as a function of reaction time (typically for 10 h). The time-averaged scattering intensity, $\langle I \rangle_T$, and its time-averaged intensity correlation function, $g^{(2)}(\tau) - 1$, were obtained with an acquisition time of 30 s for each run. Note that the data thus obtained represent time averages characteristic of the scattering volume. They may be different from ensemble averages of the macroscopic sample since the sample becomes non-ergodic during gelation.

The gels were kept in the cuvettes for 1 week, after which the reaction was considered complete and the gels were denoted as fully cured gels. DLS measurements were then performed at approx. 50 randomly selected scattering volumes to obtain ensemble averages. The scattering angle was also varied.

3. Results and discussion

Shibayama and Norisuye [34] have shown that in time-resolved DLS experiments on the gelation process, the gel point can be recognized by the following four features: (1) appearance of a speckle pattern in the scattering intensity, (2) appearance of a power-law behavior in the intensity time correlation function (ICF), (3) a specific broadening of the distribution function $G(I)$, and (4) a noticeable suppression of the initial amplitude of ICF.

When the polymer concentration is rather low, macroscopic gelation cannot take place and only microgels are formed. This was observed for sample G1-30 and has been discussed in detail in a previous paper [41]. The minimum concentration required for the formation of a continuous network is practically identical to the overlap concentration c^* , where the state of the solution changes from isolated to overlapping coils. The latter is just around 0.01 g/mL for the system under study.

Time-dependent DLS data on sample G1-30 are shown in Figs. 1 and 2 to emphasize the distinct difference between a gelling and a non-gelling system. The time-averaged scattering intensity increases smoothly over some 15 h from about 10 kHz to 50 kHz, while the reaction between terephthalaldehyde and the functionalized polymer is proceeding. Concurrently, the initial amplitude of the ICF, σ_I^2 , seems to rise slightly from 0.8 to 0.95. In our view, this latter change is negligible and has no physical meaning. It is probably due to the fact that the scattering intensity at the beginning of the reaction is rather small, overemphasizing coherence problems and leading to poorer correlation functions. The important fact is that σ_I^2 is close to unity and remains so throughout the reaction, which is indicative of an ergodic system.

The ICFs shown in Fig. 2 are slightly shifted to longer decay times with increasing extent of reaction, but they still

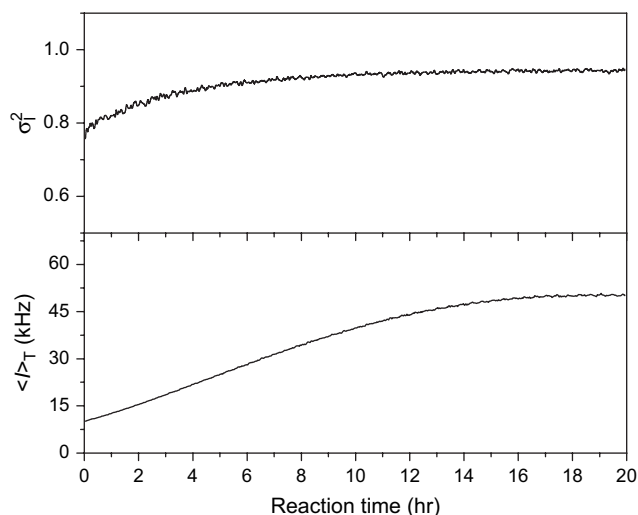


Fig. 1. Variation of the scattering intensity, $\langle I \rangle_T$, and the initial amplitude of ICF, σ_1^2 , for sample G1-30 during cross-linking reaction.

decay essentially to zero and the overall change is rather small as compared to the gelling systems to be discussed below. If only intramolecular cross-links were formed, one would expect a tendency to smaller decay times because the polymer coils would be shrinking with the formation of cross-links. The actually observed shift to larger decay times indicates that intermolecular reactions play an important role, resulting in clusters made up of several polymer molecules (microgel particles). This is expected because the concentration is close to the chain overlap. On average, the clusters should be not larger than 5–10 times the size of a single polymer coil (in linear dimensions), since the decay time changes less than one decade. The CONTIN analysis provides a distribution function of correlation lengths with two maxima, one around 10 nm and the other around 100 nm. The second maximum becomes more pronounced with increasing reaction time. The

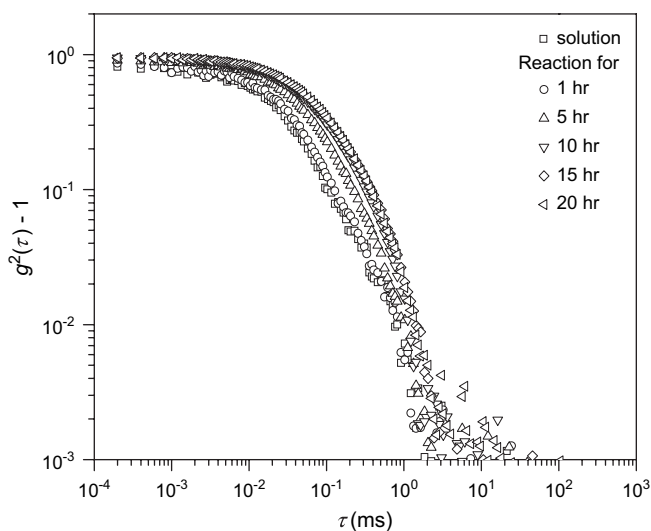


Fig. 2. Change of the time-average intensity correlation functions during the cross-linking reaction for sample G1-30.

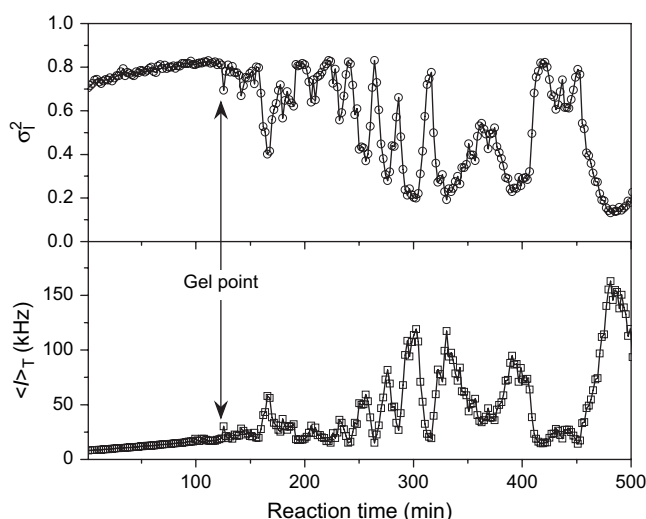


Fig. 3. Variation of the scattering intensity, $\langle I \rangle_T$, and the initial amplitude of ICF, σ_1^2 , for sample G2-30 during the gelation process.

relaxation rate, Γ , is proportional to q^2 indicating diffusional dynamics.

Fig. 3 shows a plot like Fig. 1, but for sample G2-30 as an example of the fundamentally different behavior of a gelling system. The scattering intensity increases gradually in the time regime $t < 125$ min, similar to what was observed with sample G1-30. However, from $t = 125$ min extensive fluctuations appear for both the scattering intensity and the initial amplitude of the ICFs. This behavior is characteristic of gel formation and the concomitant loss of ergodicity [54]. At a reaction time of 125 min, the growth of branched chains or clusters has reached a point where continuous structures spanning the whole system appear. The gel point or, more specifically, the gelation time can thus be estimated from dynamic light scattering measurements.

The data shown in Fig. 3 were obtained by probing one particular scattering volume as a function of time. Since the system becomes non-ergodic when the reaction time exceeds 125 min, inspection of other scattering volumes within the same macroscopic sample results in different patterns of fluctuations, but fluctuations begin to appear at ~ 125 min in each case. The fluctuations observed as a function of time for a particular scattering volume must be distinguished from the so-called speckle pattern representing fluctuations in space with time being constant or irrelevant because reactions do not occur. The latter represent variations around an ensemble average, while in the present study the excursions are a sign of the progressing cross-linking reaction.

A comparison of the time-dependent variations of the (time-averaged) scattering intensity and of the initial amplitude of the ICF (Fig. 3) reveals that both occur almost simultaneously, but in opposite directions. This fact is in accord with the notion that the scattering intensity from a gel consists of a static contribution and a dynamic contribution. The static contribution accounts for the peak intensities observed. When the static contribution is high, the initial amplitude of the ICF representing the dynamic contribution has to be low, and vice versa.

The first appearance of fluctuations in the scattering intensity and the initial amplitude of the ICF are indicative of gelation, and it was thus determined how the gelation times depend on polymer and cross-linker concentrations. The results are depicted in Fig. 4. The higher the polymer concentration or cross-linker concentration, the shorter is the time to reach the gel point. The gelation times stretch from 10 min to more than 100 min as a result of moderate variations of the respective concentrations. This strong dependency may be partly due to the variation of reaction kinetics, but the major influence seems to arise from the fact that the extent of reaction required for gelation is a strong function of polymer or cross-linker concentration.

Some typical ICFs obtained during the gelation process for sample G2-30 are shown in Fig. 5. The graph was split into two because the features before and after the gel point are quite different. At times $t < 125$ min (Fig. 5a), the ICFs exhibit

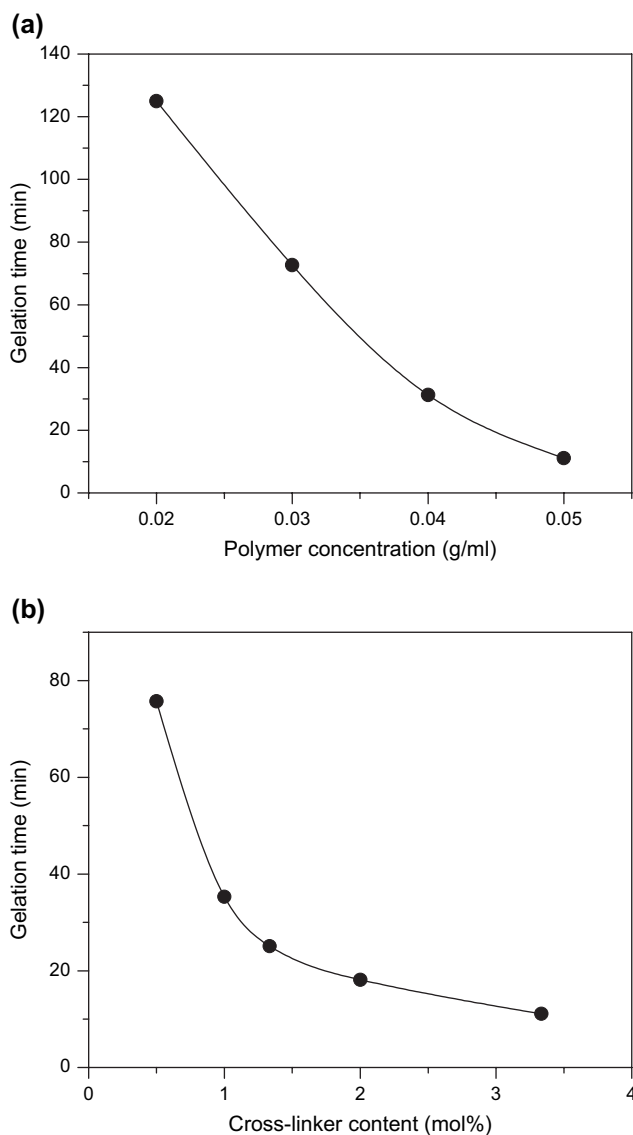


Fig. 4. Gelation time as a function of (a) polymer concentration and (b) cross-linker content.

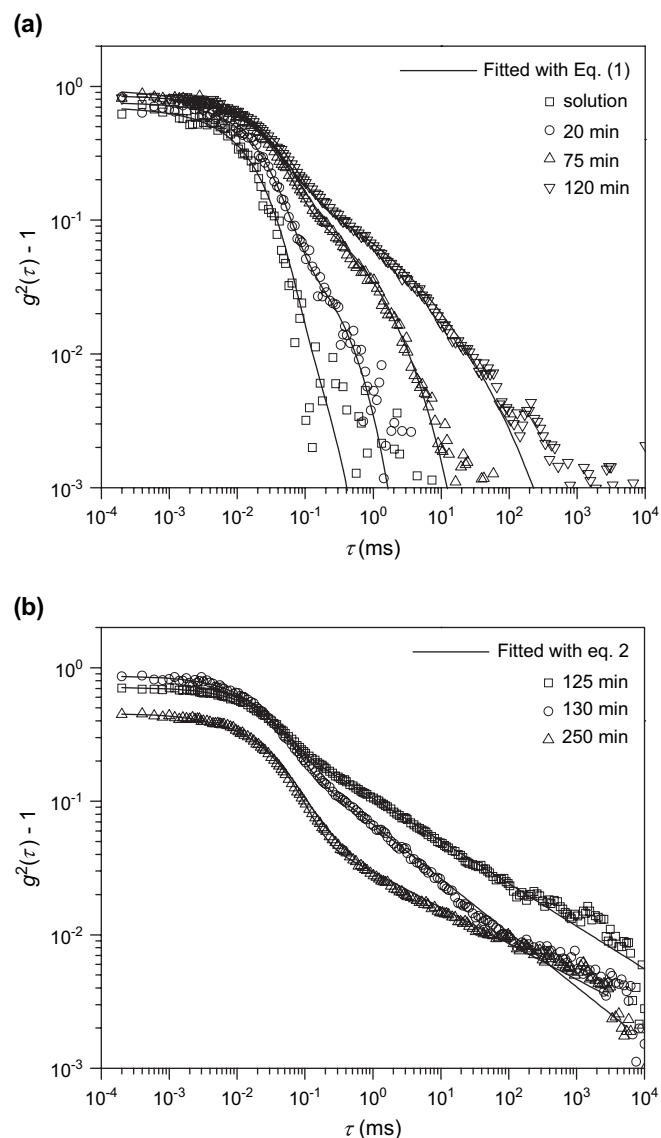


Fig. 5. Change of the time-average intensity correlation functions during the gelation process for sample G2-30: (a) before and (b) after the gel point.

two decay times: a fast diffusive mode with a diffusion coefficient (time constant) close to that of the corresponding semidilute solution, and a slow mode which is possibly due to the relaxation of clusters or branched structures interpenetrating the entangled linear chains. Following Martin et al., this time dependence can be described by a squared sum of a single exponential and a stretched exponential [Eq. (1)] [33].

$$g_T^{(2)}(\tau) - 1 \approx \sigma_1^2 \left\{ A \exp(-\tau/\tau_f) + (1 - A) \exp\left[-(\tau/\tau_s)^\beta\right] \right\}^2 \quad \text{sol state} \quad (1)$$

τ_f and τ_s are the relaxation times of the fast and slow components, respectively, and β is the exponent of the stretched exponential, while A and $1 - A$ represent the fractional contributions of the two processes. It is seen that the fitted curves shown as solid lines represent the data quite well.

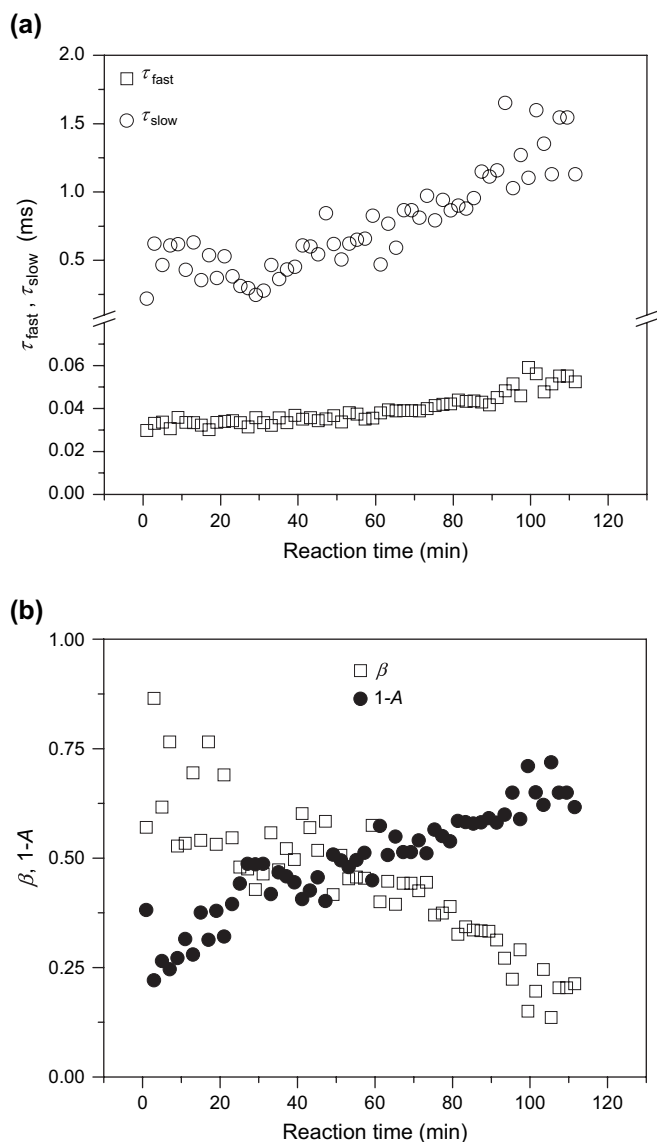


Fig. 6. (a) Variations of characteristic decay times of the fast and slow modes, τ_f and τ_s , respectively. (b) Fraction of the slow mode, $1 - A$, and the exponent of the stretched exponential, β , as a function of reaction time before the gel point; sample G2-30.

Fig. 6a shows the evolution of the decay times of the two processes in the pregel regime. The relaxation time of the fast mode rises slightly from 30 to 50 μ s as the system is approaching the gel point, while τ_s exhibits a more noticeable change from 500 to about 1500 μ s. Simultaneously, the contribution of the slow mode, $(1 - A)$, increases from <0.25 to more than 0.6, and its dispersion broadens considerably with β decreasing from 0.8 to 0.2 (Fig. 6b). These observations emphasize that the slow mode is sensitive to the long-range connectivity developing during gelation, while the fast mode is not. The fast relaxation represents the local motion of subchains (or blobs) between entanglements, and cross-linking has hardly any effect thereon. The slow mode, on the other hand, is due to the diffusion of the entire branched chains or clusters. These appear and grow bigger with increasing extent of cross-linking,

leading to an augmentation of the slow process and a simultaneous slowdown.

The ICFs measured after the gel point (Fig. 5b) cannot be modeled by Eq. (1), because they feature a long-time tailing. The combination of a single exponential and a power-law decay according to Eq. (2) is much better suited in this case (cf. Ref. [33]):

$$g_1^{(2)}(\tau) - 1 \approx \sigma_1^2 \left\{ A \exp(-\tau/\tau_f) + (1 - A)(1 + \tau/\tau^*)^{m/2} \right\}^2 \text{ gel state} \quad (2)$$

Here, τ^* is the characteristic time where the power-law behavior begins. Note that the prefactors, A and $(1 - A)$, in Eqs. (1) and (2) should not be compared because the relaxation of the stretched exponential overlaps considerably with the fast relaxation while the power-law term does not. The change of the shape of ICFs from a stretched exponential to a power-law behavior is well known [32–34,46,47,55–57], and indicates that the branched chains or clusters are interconnected to form a continuous gel.

Fig. 5b reveals that there is quite some variation with regard to the slope of the linear tail, m , of the ICFs. The three curves shown, which represent an arbitrary choice out of some 50 ICFs, have exponents -0.31 (125 min), -0.39 (130 min), and -0.24 (250 min). The analysis of all the ICFs obtained for sample G2-30 as a function of time yields a mean slope of -0.25 with a standard variation of ± 0.06 . No perceptible dependence on curing time was detected, hence the slope is the same for the incipient gel and for the fully cured system. Furthermore, the statistical variation of the slope is not correlated with the variation of the scattering intensity or the initial amplitude of the ICFs. Lastly, no q -dependence of the power-law exponent was observed.

The results obtained for the other samples are very similar. Fig. 7 shows a compilation of the exponents as a function of polymer concentration (Fig. 7a) and cross-linker concentration (Fig. 7b). Two averages are shown for each gel: one represents the average slope of about 10 successive measurements made right after the gel point, in a time span of about 5 min. The other one represents the ensemble average of the fully cured gels, obtained by probing at least 50 different scattering volumes. The virtual identity of the two averages and the fact that the statistical variations are alike, demonstrate that m is unaffected by the non-ergodicity of the system. A value of $m = -0.25 \pm 0.06$ seems to be universal for the cross-linking process under study, i.e. the random cross-linking of existent macromolecules in semi-dilute solution.

The power-law exponent m characterizing the slope of the long-time tail of the ICF has been related to the exponent n observed in viscoelasticity at the gel point, where $G'(\omega) \sim G''(\omega) \sim \omega^n$: $n = 1 + m$ [3,32]. The physical origin of m was discussed by Adam and Lairez [3] and related to the fractal structure of the gels or aggregates [17,22,23]. This simple relationship leads to $n = 0.75 \pm 0.06$ for our system. Note that we did not perform rheological measurements, and we discuss only the data derived from DLS.

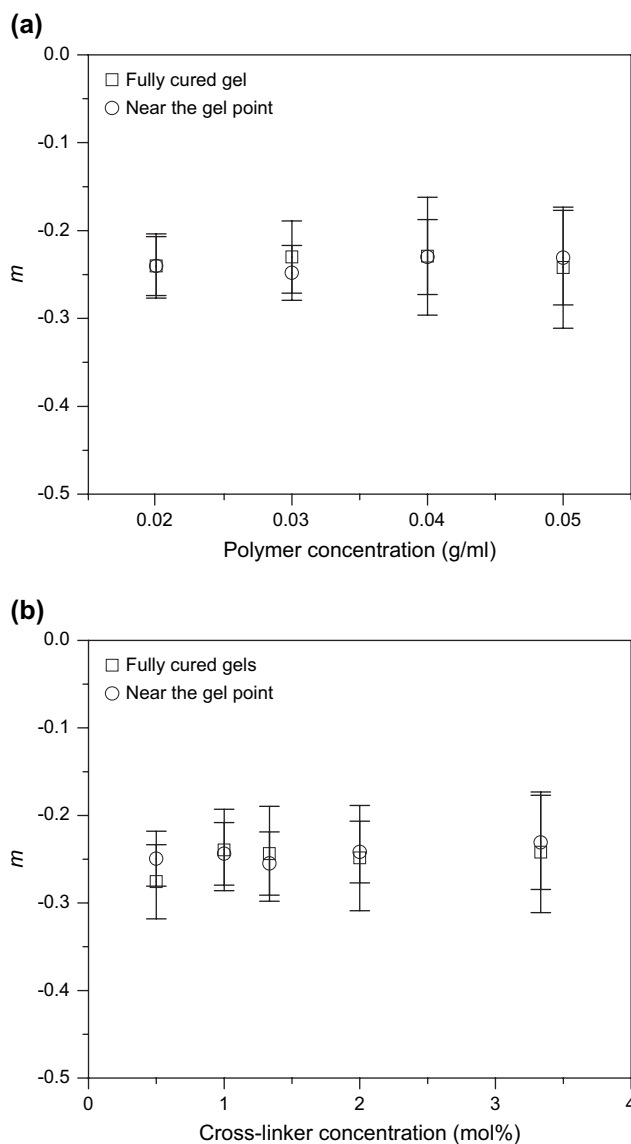


Fig. 7. Variation of m near the gel point and for the fully cured polystyrene gels as a function of (a) polymer concentration and (b) cross-linker content.

Based on the assumption of isomorphism between the complex modulus and the electrical conductivity of a percolation network with randomly distributed resistors and capacitors, a value of $n = 0.72$ was predicted by de Gennes [58], which is pretty close to the experimental value found in this work. Muthukumar suggested that the screening of excluded volume can lead to significant changes in the scaling exponent. For the fully screened case [21–24], Eq. (3)

$$n = \frac{d}{d_f + 2} \quad (3)$$

should hold, where d ($=3$) is the space dimension and d_f is the fractal dimension of the polymer clusters. With the experimentally found $n = 0.75$, this leads to $d_f = 2$. On the other hand, when only partial screening is considered [24], Eq. (4)

$$n = \frac{d(d + 2 - 2d_f)}{2(d + 2 - d_f)} \quad (4)$$

leads to $d_f = 5/3$. This latter value corresponds just to the fractal dimension of a linear chain in a good solvent and therefore seems to be rather small. Regardless of whether Eq. (3) or Eq. (4) is more appropriate to comprise the properties of the system, the low fractal dimension deduced from the DLS data, $5/3 \leq d_f \leq 2$, implies that the gel is made up of very loosely branched or cross-linked chains. The degree of branching as reflected in d_f seems not to change appreciably from the gel point to completion of the cross-linking reaction.

What appears more significant than the absolute value of the exponent (or the fractal dimension deduced therefrom) is the fact that there is no perceptible change with polymer concentration or cross-linker concentration within the inspected range. Screening of excluded volume might be expected to depend distinctly on concentration. The experimental results indicate that this has no significant effect on our system, i.e. the cross-linking of existent macromolecules in semi-dilute solution.

4. Conclusions

The random cross-linking of appropriately functionalized polystyrene in semi-dilute toluene solution was studied by DLS. Macroscopic gelation occurred from concentrations as low as 0.02 g/mL. The gelation time, determined from the first appearance of fluctuations of the scattering intensity and the initial amplitude of the ICF, decreases markedly with an increase of polymer concentration or cross-linker content.

After the gel point, the ICFs display a characteristic power-law decay which remains existent for the fully cured gels. The power-law exponent, $n = 0.75 \pm 0.06$, does not change with (i) extent of reaction, (ii) polymer concentration, and (iii) cross-linker concentration (within the inspected ranges). This universal behavior is different from what was reported for other gelling systems such as chemical gels made by cross-linking copolymerization [43,44], physical gels [48–50,52,53], or silica gels [32,33,46,47] obtained by hydrolytic condensation of alkoxides. In all these cases, a range of exponents from 0.4 up to 0.75 was found, with a marked dependence on preparation conditions and extent of reaction. The observation that the power-law exponent in the present study dealing with random cross-linking of existent macromolecules is insensitive to these parameters might be due to the fact that the system is semi-dilute throughout the reaction. Thus screening of free volume and hydrodynamic screening remain essentially unchanged.

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